

Low-Cost Pt-Free Counter Electrode Catalysts in Dye-Sensitized Solar Cells

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Abstract Dye-sensitized solar cells (DSCs) are potential candidates to silicon solar cells due to their merits of simple fabrication procedure, low-cost, and good plasticity. Till date, great advances have been achieved in the design of dyes, redox couples, and counter electrode (CE) catalysts for DSCs and the highest energy conversion efficiency is up to 12.3 %. In this part, our attention focuses on CE catalysts. Besides Pt, carbon materials, conductive polymers, transition metal compounds (carbides, nitrides, oxides, sulfides, phosphides, selenides), and composite catalysts, denoted as Pt-free catalysts, have been introduced into DSCs as CE catalysts. In the following sections, we give a summary of Pt-free CE catalysts and highlight the advantages and disadvantages of each variety of Pt-free catalysts.

1 Carbon materials

Carbon materials possess the merits of low-cost, high catalytic activity and electric conductivity, good thermal stability, and corrosion resistance. These merits make carbon materials ideal substitutes to the expensive Pt catalyst in many fields. In the DSCs system, they have been widely used as counter electrode (CE) catalysts. Takahashi et al. used activated carbon (Ca), a type of amorphous carbon with a

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diamond structure, as a CE catalyst in DSCs [1]. The photovoltaic performance is positively correlated with roughness factor of the Ca CE. In contrast, the roughness factor is negatively correlated with the charge-transfer resistance (R_{ct}) in the CE/electrolyte interface. The DSC using Ca CE showed power conversion efficiency (PCE) of 3.89 %, slightly lower than that of the DSC using Pt CE (Pt-DSC) which produced a PCE of 4.30 %. Grätzel and Kay introduced graphite and carbon black (Cb) into a monolithic DSC as the CE catalyst, and the DSC produced a PCE of 6.7 % [2]. In this kind of carbon CE, graphite improved the lateral conductivity of the CE and Cb granted the CE a large surface area, resulting in high catalytic activity. They also found that the thickness of Cb film affected the fill factor (FF) and PCE significantly, while open-circuit voltage (V_{oc}) and short-circuit current density (J_{sc}) varied very little as the Cb film thickness increased [3]. The DSC using Cb CE with 14.47 μm thickness produced the highest PCE of 9.1 %.

Zou et al. fabricated fiber-shaped DSCs using carbon fiber (Cf) as CE and the DSC gave a PCE of 2.7 % [4]. Wang et al. introduced mesoporous carbon (Cm) into DSCs as CE, yielding a PCE of 6.18 % [5]. Ramasamy et al. prepared ferrocene-derivatized large pore size mesocellular carbon foam (Fe-MCF-C) used as CE catalyst in a DSC which gave a PCE of 7.89 % [6]. Carbon nanotubes (CNTs) can be divided into single-wall CNTs (SNTs), double-wall CNTs (DNTs), and multi-wall CNTs (MNTs) and they can be designed as a semiconductor or metallic material according to the varied chiralities [7]. Using CNTs to replace Pt can endow with CE the following advantages: nanoscaled transfer channels, large specific surface area, low-cost, high catalytic activity, and light weight. The DSC using SNTs as CE yielded a PCE of 4.5 % [8]. Lee et al. applied MNTs as CE in the DSCs. The DSCs using MNTs and Pt CEs showed PCE of 7.67 % (MNTs) and 7.83 % (Pt) [9]. The high density of the defect-rich edge planes of MNTs guarantees its high catalytic activity. The technique adopted to prepare CNTs CEs is crucial for obtaining high catalytic activity. Kim et al. prepared CNTs CEs with screen printing (SP) technique and chemical vapor deposition (CVD) technique. The CNTs (SP) were randomly oriented and woven into each other, whereas the CNTs (CVD) were grown directly on the substrate. The DSC using the CNTs (SP) CE gave a PCE of 8.03 %, while the well aligned CNTs CE made the PCE value reach to 10.04 % [10]. The advantages of CNTs (CVD) CE can be attributed to high conductivity because of the well-aligned arrangement. Besides SP and CVD techniques, spraying technique can be used to fabricate CNTs CE [11]. The CNTs film thickness was regulated by spraying time and the impact of CNTs film thickness (or spray time) on the performance of DSCs was also investigated. As the time increased from 5 to 30 s, the J_{sc} and FF increased rapidly and the PCE value improved from 0.68 to 3.39 %. The highest PCE of 7.59 % was obtained at spraying time of 200 s. In their work, the PCE increased continuously with spraying time (0–200 s). According to our experiences, there should exist an optimal spraying time (i.e., thickness).

Zhu et al. attempted to find the differences between SNTs, DNTs, and MNTs as CEs under the same conditions [12]. The DSC using SNTs CE performed best (1.46 %), compared with the other two DSCs based on DNTs (0.45 %) and MNTs

(0.62 %) CEs. The highest catalytic activity of the SNTs for regeneration of the I_3^-/I^- redox couple was caused by the one-dimensional nano-feature which provides better electron transport. Moreover, the impurities (iron, amorphous carbon) in SNTs can influence the catalytic performance dramatically. For example, the DSC using purified SNTs CE yielded a PCE of 1.46 %, while the DSC using raw SNTs CE gave a poor PCE of 0.57 %. This difference caused by catalyst poisoning, because the catalytic sites was occupied by impurities. The purification process in turn introduced many oxygen-function groups that formed new catalytic sites.

Graphene is a single layer of two-dimensional graphite with advantages of high conductivity, transparency, hardness, and corrosion resistance, and it has become a hot research topic in various fields. Grätzel et al. used graphene to fabricate optically transparent CE for DSCs [13]. It was observed that graphene CE was more suitable for ionic liquid solvent than the traditional organic solvent. The R_{ct} value of the ionic solvent is much smaller than the traditional solvent, which indicates that the mechanism for regeneration of I_3^-/I^- in the graphene surface is determined by solution events rather than viscosity. The catalytic activity of graphene is proportional to the content of active sites (edge defects and oxide groups). Finally, they suggested that graphene might be a promising substitute for Pt and also for the expensive FTO conductive layer. Aksay et al. found the catalytic activity was correlated with the concentration of the oxide group and the C/O ratio strongly influenced the catalytic activity [14]. When the C/O ratio was up to 13, graphene CE showed the highest catalytic activity, and the DSC gave a PCE of 5.0 %, close to that of the DSC using Pt CE (5.5 %). Jeon et al. synthesized graphene by reducing graphite oxide. It was found that the catalytic activity increased as the number of oxygen functional groups decreased [15]. Combining with previous results [14], we thought that there existed an optimum number of oxygen functional groups for graphene to achieve optimal catalytic activity. The PCE values for the DSCs in the above mentioned works were all less than 6 %, leaving much room for improvement by modifying the concentration of the oxygen functional groups or lattice defect. Nevertheless, to fully evaluate these statements requires more research.

Ma group compared the properties of nine kinds of carbon materials containing Ca, Cb, conductive carbon (Cc), carbon dye (Cd), Cf, CNTs, Ordered mesoporous carbon (Com), discard toner (Cp), and C_{60} at the same conditions [16]. Com is made of rows of well-ordered carbon walls with a width of approximate 10 nm. This carbon wall configuration forms many channels in the CE body which can increase the contact area of the electrolyte and the CE surface and this configuration can promote electrolyte diffusion. The DSC using Com CE yielded a high PCE of 7.5 %, the same as the DSC using Pt CE. The traditional carbon materials (Ca, Cb, Cc, CNTs, and Cf) showed decent catalytic activity and the DSCs yielded PCE values from 6.3 % to 7.0 %. Cd showed catalytic activity as high as Com, and the DSC gave a PCE of 7.5 %. Even the DSC using Cp CE showed a decent PCE of 4.3 %. When impure C_{60} CE was used in DSC, a low PCE of 2.8 % was achieved. As predicted, C_{60} should perform as effectively as the other carbon materials due to its superior electrical conductivity, stability, and other attributes. The low activity may be caused by impurities, which may result in catalyst poisoning. They indicated that

the main disadvantage of carbon CEs is the poor bonding strength between the carbon films and the substrate. Adding TiO_2 can improve bonding strength between carbon films and the substrate, but it was found that adding too much TiO_2 can lower the catalytic activity, because of the bad conductivity of TiO_2 . Meanwhile, the impact of carbon film thickness on the catalytic activity has been investigated. An excessively thin carbon film can lead to insufficient catalytic activity while an excessively thick carbon film can crack and detach from the substrate. To achieve high catalytic activity, carbon film with $25\ \mu\text{m}$ thickness is appropriate. The thickness of the carbon films affects FF significantly.

Lee et al. studied the impact of carbon particle size on the catalytic activity [17]. The DSC using the nanocarbon (surface area, $100\ \text{m}^2\ \text{g}^{-1}$) CE gave a PCE of 6.73 %, much higher than the DSC using microcarbon (surface area, $0.4\ \text{m}^2\ \text{g}^{-1}$) CE. The different behavior between the two kinds of carbon materials can be attributed to the surface area and conductivity. Meng et al. prepared flexible carbon CE using Ca as the catalyst and graphite sheet as the substrate [18]. Low (series resistance) R_s and R_{ct} were obtained for this carbon CE due to high electrical conductivity of graphite and high catalytic activity of Ca. The DSC using this CE showed a PCE of 6.46 % which can match the performance of the DSC using Pt CE (6.37 %).

Carbon is indeed a qualified CEs catalyst in DSCs. However, the main disadvantage of carbon CE is still the poor bonding strength between carbon film and the substrate. This may be a potential unstable factor for long-term use. Deposited carbon film on the substrate by in situ technique could resolve this problem. Furthermore, fabricating incorporated carbon CE (carbon catalysts and carbon substrate) may be another solution. Opacity is another disadvantage of carbon CEs. We believe developing transparent carbon CEs for DSCs will become a promising research topic in the future.

2 Conductive Polymers

Transparency and flexibility are two merits for DSCs which require transparent flexible photoanode, transparent electrolyte, and transparent flexible CE. Generally, transparent flexible substrate (ITO–PET, ITO–PEN) deposited with Pt is widely used as CE. Besides Pt, conductive polymers like poly (3, 4-ethylenedioxythiophene) (PEDOT) or its derivatives can be used as CE catalysts.

PEDOT-Polystyrenesulfonate (PSS) was used as CE catalyst in quasi-solid DSCs in which this PEDOT performed better than Pt for ionic liquid electrolyte (ILE) [19]. In the EIS test, the R_{ct} value for the PEDOT–PSS/ILE was much lower than Pt/ILE. However, in the organic liquid electrolyte (OLE), the result was opposite. Yanagida et al. gave a detailed explanation for the aforementioned phenomenon [20]. ILE needs high I_2 concentration due to high viscosity and low conductivity. Therefore, the porous PEDOT CE performed better than Pt in ILE. Gîrțu et al. indicated that there existed charge transfer between PEDOT and iodide redox couple by X-ray photoelectron spectroscopy (XPS) [21]. This phenomenon

was also observed by Biallozor et al. through CV test [22]. Apart from PEDOT, Poly (3,3-diethyl-3,4-dihydro-2*H*-thieno-[3,4-*b*] [1, 4] dioxepine) (PProDOT-Et₂) also can be used as CE catalyst for DSCs [23]. PProDOT-Et₂ film was directly deposited on FTO substrate by electropolymerization with various charge capacities (10, 20, 40, 80, 120, 160, 200 mC cm⁻²). When the deposited charge capacity reached 40 mC cm⁻², the PProDOT-Et₂ film produced the largest active surface area, contributing to the high catalytic activity similar to Pt. The DSC using this polymer CE yielded a PCE of 5.20 %.

Wu et al. prepared polypyrrole nanoparticles (PPy) with particle size ranging from 40 to 60 nm [24]. The DSC using PPy CE showed a PCE of 7.66 %, higher than the photovoltaic performance of the DSC using Pt CE (6.90 %). Xia et al. fabricated PPy CEs on FTO glass with vapor phase polymerization (VPP) and electropolymerization (EP) techniques [25]. The PPy particle (VPP) size is 100–150 nm and the PPy (EP) has a larger particle size of 200–300 nm. The DSCs using these PPy CEs yielded PCE of 3.4 % (VPP) and 3.2 % (EP), slightly lower than Pt-DSC (4.4 %). In addition, PPy sphere with a uniform size of 85 nm was used as CE catalyst for DSCs and decent PCE was obtained [26]. Zhao et al. prepared transparent polyaniline (PANI) CE on FTO glass for DSCs CE [27]. At front illumination, the DSC showed a PCE of 6.54 %; at rear illumination, a PCE of 4.26 % was achieved. Moreover, Wu et al. fabricated mesoporous PANI thorough an oxidative polymerization of aniline monomer as CE for DSCs and a PCE of 7.15 % was obtained [28].

Organic polymer CEs own the advantages of transparency, high catalytic activity, easy availability, and low cost. However, the stability (chemical stability, thermal stability, and photo stability) may be an adverse property for practical application. Reports on stability tests for polymer CEs are still rare.

3 Transition Metal Compounds

Early transition metal carbides, nitrides, oxides, sulfides, and phosphides exhibit Pt-like catalytic behavior. These materials have been used in the fields of CO₂ methanation, ammonia synthesis, dehydrogenation, hydrogenation, methanol oxidation, photocatalysts, gas sensors, electrochromic devices, field emitters, among others, as a replacement for the noble metal. Very recently, these compounds have been proposed to use as CE catalysts in DSCs. Next, we will give a detailed introduction.

3.1 Carbides

Ma group introduced tungsten carbide (WC) and molybdenum carbide (Mo₂C) into DSCs as CE catalysts. The DSCs using WC and Mo₂C as CEs gave PCE of 5.35 % (WC) and 5.70 % (Mo₂C), lower than the PCE of the Pt-DSC (7.89 %).

This relative lower performance stems from the large size of the two carbides Mo_2C , 300 nm; WC, 190 nm [29]. Then they synthesized nano-scaled WC and W_2C using metal-urea route. The DSCs using the nanoscaled carbides as CEs achieve high PCE of 6.68 % (W_2C) and 6.23 % (WC). Compared with the large WC particle, the nano-scaled WC showed improved catalytic activity [30]. Lee et al. prepared polymer-derived WC (WC-PD) and microwave-assisted WC (WC-MW), which have been introduced in DSCs as CE catalysts. The DSCs yielded PCE of 6.61 % (WC-PD) and 7.01 % (WC-MW), lower than that of the DSC using Pt CE (8.23 %) [31]. Moreover, Ma group did a systematic research on other transition metal carbides, such as TiC, VC, ZrC, NbC, Cr_3C_2 , and so on [32, 33]. All of the carbides give high catalytic activity except ZrC and NbC.

3.2 Nitrides

Gao et al. prepared TiN nanotubes used as CE catalyst in DSC which produced a PCE of 7.73 % [34]. Similar to TiN, MoN, WN, and Fe_2N were synthesized by nitridation of the oxide (MoO_2 , WO_3 , Fe_2O_3) precursors in ammonia atmosphere, after which the nitrides were used as CE catalysts into DSCs [35]. The DSCs gave PCE values of 5.57 % (MoN), 3.67 % (WN), 2.65 % (Fe_2N), and 6.56 % (Pt). Meanwhile, Ma et al. prepared Mo_2N and W_2N films on flexible Ti sheet as CEs for DSCs which produced PCE of 6.38 % (Mo_2N) and 5.81 % (W_2N). In addition, they also introduced ZrN, VN, NbN, CrN into DSCs, and decent results were obtained [32]. Gao et al. used surface-nitrided Ni foil as the CE in DSCs, resulting in a PCE of 5.68 %, much lower than that of the Pt-DSC (8.41 %) [36], while NiN with a mesoporous structure showed high catalytic activity and the DSC yielded a PCE of 8.31 %.

3.3 Oxides

Ma et al. observed that WO_2 and WO_3 can be used as a catalyst for the reduction of I_3^- to I^- [37]. The DSC based on WO_3 CE showed a PCE of 4.67 %. WO_2 nanorod showed excellent catalytic activity and the DSC gave a high PCE of 7.25 %, close to that of the Pt-DSC (7.57 %). Recently, they synthesized H-Nb $_2\text{O}_5$ (hexagonal), O-Nb $_2\text{O}_5$ (orthorhombic), M-Nb $_2\text{O}_5$ (monoclinic), and T-NbO $_2$ (tetragonal) and then used the four niobium oxides as CE catalysts in DSCs [38]. The DSCs showed PCE values of 5.68 % (H-Nb $_2\text{O}_5$), 4.55 % (O-Nb $_2\text{O}_5$), 5.82 % (M-Nb $_2\text{O}_5$), and 7.88 % (T-NbO $_2$). Obviously, NbO $_2$ performs best among the four niobium oxides and the crystal forms significantly affecting the catalytic activity. Xia et al. used V_2O_5 as CE in solid DSCs. The PCE of the DSC using a 10 nm thick V_2O_5 CE reached 2.0 % [39].

As we know, WO_3 , Nb_2O_5 , SnO_2 , and other oxides are widely used as photoanode semiconductor. Now, it has been proved that some oxides can be used as CE catalysts. If the oxide is used in the photoanode, the direct contact of oxide and I_3^-/I^- redox couples may cause the I_3^- to be reduced by the electrons injected in the conductive band of the oxide due to autocatalytic activity. This is to say, a number of the electrons injected in the conductive band cannot be collected by the substrate and, thus, flow into the external circuit. The autocatalytic activity of oxide can result in a large dark current density. This may be a key reason for the poor performance of the DSCs using TiO_2 -free oxides as photoanodes [40]. In addition, Ma et al. found that the catalytic activity can be enhanced significantly by sintering the oxide CEs in N_2 atmosphere [41]. The fundamental reason for the high catalytic activity of some oxides is still unclear and requires further study.

3.4 Sulfides Selenides and Phosphides

The aforementioned carbides, nitrides, and oxides all show catalytic activity for the regeneration of the redox couples in DSCs. Similarly, transition metal sulfides are expected to behave in a similar fashion. Grätzel et al. prepared CoS CE on flexible substrate and the DSC yielded a PCE of 6.5 % [42]. Co and Ni both belong to Group VIII A metals. Meng et al. prepared NiS CEs by periodic potential reversal (PR) and potentiostatic (PS) techniques. The DSCs showed PCE of 6.83 % (PR-NiS) and 3.22 % (PS-NiS) [43]. Lin et al. introduced copper zinc tin sulfide (CZTS) to DSCs system as CE. CZTS performed well for the regeneration of iodide from triiodide. The DSC using the CZTSSe CE gave a PCE of 7.37 % higher than the corresponding photovoltaic of the Pt-DSC [44]. Ma et al. introduced MoS_2 and WS_2 into DSCs as CEs [45]. MoS_2 and WS_2 showed high catalytic activity compared to Mo (or W) carbides, nitrides, and oxides and the DSCs gave high PCE of 7.59 % (MoS_2) and 7.73 % (WS_2) which can match the performance of the Pt-DSC (7.64 %). Besides sulfides, Ma et al. used Ni_5P_4 and MoP as CEs in DSCs, which showed PCE of 5.71 % (Ni_5P_4) and 4.92 % (MoP). Meanwhile, Gao et al. introduced Ni_{12}P_5 as CE in DSCs, a PCE of 3.94 % was achieved [46]. Recently, selenides of $\text{Co}_{0.85}\text{Se}$ and $\text{Ni}_{0.85}\text{Se}$ were also proposed as CEs in DSCs, and both of them showed high catalytic activity [47].

4 Composites

As the name indicates, composite CE catalysts commonly comprise two or more components such as TiN/CNTs, Pt/Carbon, Carbon/PEDOT/PSS, Carbon/ TiO_2 , CoS/PEDOT/PSS, and so forth. The advantage of this CE is, naturally, the combination of the best qualities of all components into one composite.

To achieve highly effective catalysts, Ma et al. synthesized MoC and WC imbedded in ordered mesoporous carbon (MoC-OMC, WC-OMC) by the in situ method [29]. The PCE values of the DSCs reached 8.18 % (WC-OMC) and 8.34 % (MoC-OMC), much higher than those of the DSCs using WC (5.35 %) and Mo₂C (5.70 %) CEs. Further, they prepared WO₂ and Ni₅P₄ imbedded in mesoporous carbon and both the composite CEs catalysts showed high catalytic activity [48, 49]. Gao et al. deposited TiN nanoparticles on CNTs (TiN/CNTs) and then used the composite as a CE in DSC which produced a PCE of 5.41 %, higher than both the DSCs using TiN CE (2.12 %) and pure CNTs CE (3.53 %) [50]. The high catalytic activity can be attributed to the combination of the high catalytic activity and the high electrical conductivity into one composite. This strategy can be used to design effective catalysts in the future research. Park et al. prepared W₂C/WC composite CE in DSC, resulting in a PCE of 4.2 %, still lower than that of Pt (5.22 %) [51]. Wu et al. introduced the Pt/Cb composite catalyst into DSCs. Loading 1.5 wt% Pt on Cb was enough to achieve high catalytic activity and the DSC gave a PCE of 6.72 % [52]. Ouyang et al. prepared PEDOT-PSS/CNTs and PSS/CNTs composite CEs [53]. The DSC using PEDOT-PSS/CNTs CE yielded a PCE of 6.5 %, much higher than that of the DSC using PSS/CNTs CE (3.6 %). Kang et al. used CoS/PEDOT/PSS as a composite CE catalyst, with the corresponding DSC giving a PCE of 5.4 %, comparable to that of the DSC using Pt CE (6.1 %). The high catalytic activity of this composite CE can be attributed to the synergistic catalytic effect [54]. Lin et al. synthesized MoS₂/Graphene composite as CE in a DSC, which gave a PCE of 6.04 %, slightly lower than that of the DSC using Pt CE [55].

On current evidence, prepared composite has become an effective path to achieve CE catalysts for DSCs. However, the mechanism of high catalytic activity and the roles of the catalyst and the supporter are still in dispute.

5 Summary

In sum, a series of Pt-free CE catalysts have been introduced into DSCs, each with unique advantages and disadvantages. We think that carbon material is the most potential substitute to Pt in DSCs. Organic polymers offer a promising alternative as flexible and transparent CEs. In addition, the introduction of transition metal carbides, nitrides, oxides, sulfides, selenides, and phosphides into DSCs widens the selective scope of CE catalysts remarkably. Combining two or more proper materials into one composite is an effective path to design high-efficiency catalysts for DSCs. Now, to develop low-cost Pt-free CE catalysts has become a hot research topic to reduce the cost of DSCs, which makes DSCs more competitive among various photovoltaic devices, contributing to realize the industrialization of DSCs.

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